



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> HAIR STYLING COMPOSITIONS COMPRISING ANIONIC OPTICAL BRIGHTENERS  <b>(57) Abstract</b>  Disclosed is a hair styling composition comprising: (a) an effective amount of an anionic optical brightener; (b) a fixative polymer selected from the group consisting of an amphoteric fixative polymer, an anionic fixative polymer, a nonionic fixative polymer, a silicone grafted copolymer, and mixtures thereof; wherein the 3 % aqueous solution of the fixative polymer provides a viscosity of no more than about 2,000 cps; and (c) a carrier.		

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## HAIR STYLING COMPOSITIONS COMPRISING ANIONIC OPTICAL BRIGHTENERS

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### TECHNICAL FIELD

10 The present invention relates to a hair care composition comprising optical brighteners which alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage. More specifically, the present invention relates to a hair styling composition comprising anionic optical brighteners and selected fixative polymers.

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### BACKGROUND

The desire to regain the natural color and shine of damaged hair and the desire to alter the color of the hair to be more appealing are widely held. Damaged hair is perceived by the consumer as unfavorable appearances and less manageability of the hair. Such unfavorable appearances include alteration and fading of original color, less shine, and less luster.

20 A common way for alleviating the unfavorable appearances of damaged hair and to achieve appealing hair color is to dye the hair to the color desired. Dyeing the hair would provide the consumer with a stable color of hair for a relatively long period. However, dyeing the hair is generally time-consuming, cumbersome, and messy. Dyestuff may also be chemically harsh to the hair, scalp, and skin. The hair can be further damaged by dyeing. Thus, hair dye products are not suitable for daily use. Further, dyeing can leave the hair with a dull appearance, making the hair look less shiny.

30 Based on the foregoing, there is a need for a hair composition which can be used daily and which can alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage.

Use of optical brighteners, or compounds otherwise described by names such as fluorescent whitening agents, fluorescent brighteners, or fluorescent dyes, in the hair care field has been known in the art, such as in United States Patent 3,658,985, United States Patent 4,312,855, Canadian Patent 1,255,603,

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United States Patent 3,577,528, Great Britain Patent Specification 1,328,108, South African Application 676,049, European Publication 87,060, and Great Britain Patent Specification 2,307,639.

5 Hair fixative polymers with different charge types are known to be useful in achieving and maintaining a desired hair style. However, when optical brighteners with a charge are mixed with hair fixative polymers of the opposite charge in a liquid media, it forms an insoluble complex, which could cause incompatibility and/or instability in the formulation. Thus, there is a desire to provide a stable hair styling composition comprising optical brighteners with a  
10 charge.

None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY

15 The present invention is directed to a hair styling composition comprising: (a) an effective amount of an anionic optical brightener; (b) a fixative polymer selected from the group consisting of an amphoteric fixative polymer, a nonionic fixative polymer, an anionic fixative polymer, a silicone grafted polymer, and mixtures thereof; wherein the 3% aqueous solution of the hair fixative polymer  
20 provides a viscosity of no more than about 2,000 cps; and (c) a carrier.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

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### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

30 All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties.

- 5 Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

#### ANIONIC OPTICAL BRIGHTENERS

Optical brighteners are compounds which absorb ultraviolet light and re-emit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

When applied to hair via suitable vehicles, optical brighteners herein provide benefits to the hair in three areas. First, optical brighteners herein alter the color of the hair by emitting light in the visible range. Second, optical brighteners herein enhance the shine of the hair by emitting light in the visible range. Third, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet light.

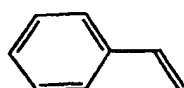
Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. Optical brighteners can be classified according to their charge type. Anionic optical brighteners useful in the present invention are those bearing a negatively charged polar group. Four types of ionized groups can be employed in anionic optical brighteners: carboxylate, sulfate, sulfonate, and phosphate. Anionic optical brighteners can be further classified according to their base structures, as

described hereafter. Preferable anionic optical brighteners herein include polystyrylstilbenes, triazinstilbenes, coumarins, triazoles, and pyrazolines.

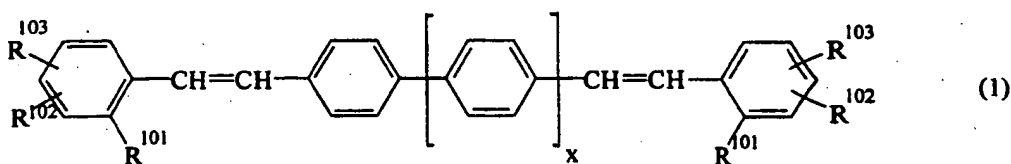
Preferably, anionic optical brighteners herein are included in the hair care composition of the present invention at a level by weight of from about 0.001% to about 20%, more preferably from about 0.01% to about 10%.

### Polystyrylstilbenes

Polystyrylstilbenes are a class of compounds having two or more of the following base structure:



Polystyrylstilbenes useful in the present invention include those having formulae (1):



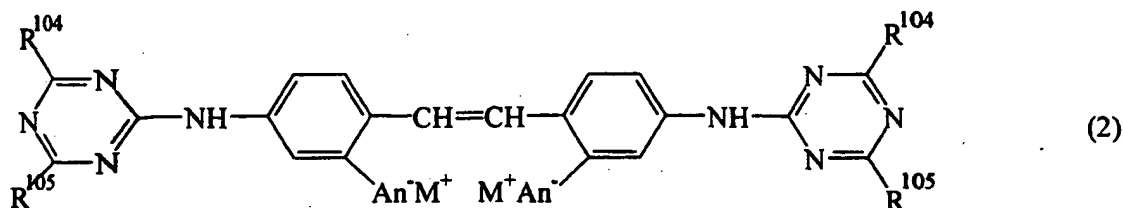
wherein  $R^{101}$  is H, OH,  $SO_3M$ , COOM,  $OSO_3M$ ,  $OPO(OH)OM$ , wherein M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- $C_1$ - $C_{30}$ -alkylammonium, mono-, di- or tri- $C_1$ - $C_{30}$ -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of  $C_1$ - $C_{30}$ -alkyl and  $C_1$ - $C_{30}$ -hydroxyalkyl groups; or  $SO_2N(C_1-C_{30}-alkyl)_2$ ,  $O-(C_1-C_{30}-alkyl)$ , CN, Cl,  $COO(C_1-C_{30}-alkyl)$ , or  $CON(C_1-C_{30}-alkyl)_2$ , CN, or alkyl of 1 to 30 carbons,  $R^{102}$  and  $R^{103}$ , independently, are  $SO_3M$ , COOM,  $OSO_3M$ ,  $OPO(OH)OM$ , wherein M is as previously defined; and x is 0 or 1; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably x is 1,  $R^{101}$  is  $SO_3Na$  and  $R^{102}$  and  $R^{103}$  are H; wherein the compound has a trans-coplanar orientation.

Suitable polystyrylstilbenes include disodium-1,4-bis(2-sulfoethyl) bisphenyl (C.I. Fluorescent Brightener 351) with tradename Tinopal CBS-X available from Ciba Specialty Chemicals.

### Triazinstilbenes

Triazinstilbenes are a class of compounds having both triazin and stilbene structures in the same molecule.

Triazinstilbenes useful in the present invention include those having formulae (2):

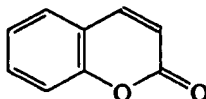


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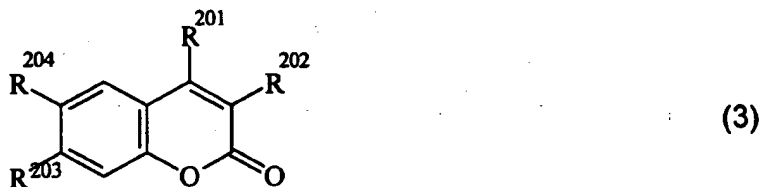
wherein  $R^{104}$  and  $R^{105}$ , independently, are  $-OCH_3$  or  $-Cl$ ; and  $An^-$  is an anion of carboxylate, sulfate, sulfonate, or phosphate, and  $M$  is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably the compound has a trans-coplanar orientation.

#### 10 Coumarins

Coumarins are a class of compounds having the following basic structure:



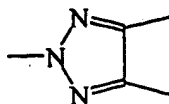
15 Coumarins useful in the present invention include those having formulae (3):



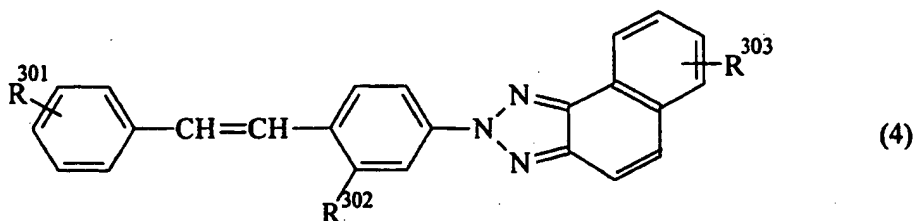
wherein  $R^{201}$  is  $(CH_2)_{1-4}COOM$ ,  $(CH_2)_{1-4}SO_3M$ ,  $(CH_2)_{1-4}OSO_3M$ ,  $(CH_2)_{1-4}OPO(OH)OM$ , wherein  $M$  is as previously defined;  $R^{202}$  is H, phenyl,  $COO-C_1-C_{30}$ -alkyl, glucose, and  $R^{203}$  is OH, or  $O-C_1-C_{30}$ -alkyl, and  $R^{204}$  is OH or  $O-C_1-C_{30}$  alkyl, glycoside.

#### 20 Triazoles

Triazoles are a class of compounds having the following base structure:

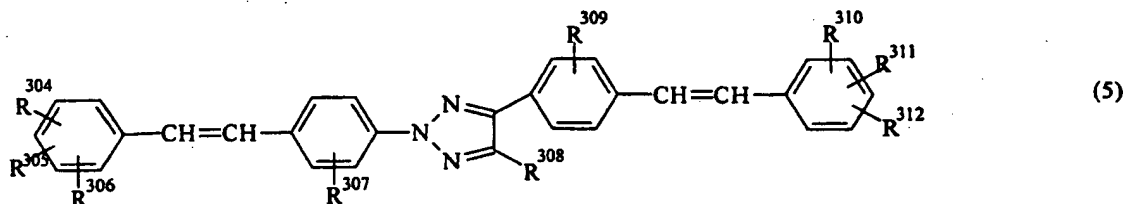


Triazoles useful in the present inventions include those having formulae (4) and (5):



- 5 wherein  $R^{301}$  is H or Cl;  $R^{302}$  is  $SO_3M$ ,  $COOM$ ,  $OSO_3M$ ,  $OPO(OH)OM$ ;  $R^{303}$  is H or  $SO_3M$ ; and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably  $R^{301}$  and  $R^{303}$  are H and  $R^{302}$  is  $SO_3M$  in which M is Na; wherein the compound has a trans-coplanar orientation;

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- wherein each of  $R^{304}$  and  $R^{310}$  independently represents  $SO_3M$ ,  $COOM$ ,  $OSO_3M$ ,  $OPO(OH)OM$ , wherein M is as previously defined, each of  $R^{305}$  and  $R^{311}$  independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with  $R^{304}$  and  $R^{310}$  represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of  $R^{306}$  and  $R^{312}$  independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of  $R^{307}$  and  $R^{309}$  independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, esters or amides thereof, or a carboxylic acid group or the salts, esters or amides thereof, and  $R^{308}$  independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, sulfonic acid groups, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be

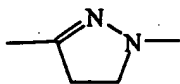


substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;

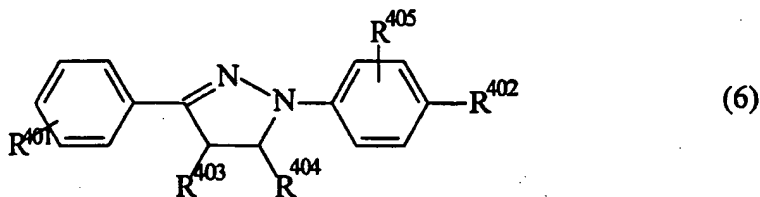
Suitable triazoles include 2-(4-styryl-3-sulphophenyl)-2H-naphtho[1,2-d] triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

#### Pyrazolines

Pyrazolines are a class of compounds having the following base structure:

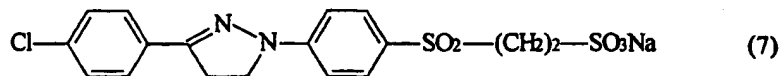


Pyrazolines useful in the present invention include those having formulae (6) and (7):



wherein R<sup>401</sup> is H or Cl, R<sup>402</sup> is SO<sub>3</sub>M, COOM, OSO<sub>3</sub>M, or OPO(OH)OM, R<sup>403</sup> and R<sup>404</sup> are the same or different and each is H, C<sub>1</sub>-C<sub>30</sub>alkyl or phenyl and R<sup>405</sup> is H or Cl; and M is as previously defined, preferably R<sup>401</sup> is Cl, R<sup>402</sup> is

SO<sub>3</sub>M wherein M is as previously defined, and R<sup>403</sup>, R<sup>404</sup> and R<sup>405</sup>, independently, are H; and



Suitable pyrazolines include 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-pyrazoline.

#### FIXATIVE POLYMERS

The fixative polymers useful herein are those which provide a styling or setting benefit to the hair, and are selected from the group consisting of amphoteric fixative polymers, anionic fixative polymers, nonionic fixative polymers, silicone grafted copolymers, and mixtures thereof. The fixative polymers in this section can be distinguished from the conditioning agent polymers and thickening polymers as mentioned below in that they have a film-forming characteristic, and that the 3% aqueous solution of fixative polymers herein provide a viscosity of no more than about 2,000 cps.

Anionic optical brighteners of the present invention provide benefits to the hair by depositing on the surface of the hair. Generally, styling compositions are liquid based. Thus, it is desired that the formulation containing the anionic optical brightener can effectively deliver the anionic optical brightener to the hair in liquid media. When anionic optical brighteners are mixed with cationic fixative polymers, it may form an insoluble complex, or may cause incompatibility and/or instability in the formulation. By selecting the fixative polymers from the group consisting of amphoteric fixative polymers, anionic fixative polymers, nonionic fixative polymers, silicone grafted copolymers, and mixtures thereof, a styling composition which can effectively deliver the anionic optical brightener and also provide good styling benefits is obtained.

It is known in the art that combining fixative polymers may enhance the benefits and/or alleviate the shortcomings of the combined fixative polymers. Preferred fixative polymer combinations of the present invention include the combination of betainized amphoteric fixative polymer and non-betainized amphoteric fixative polymer, and the combination of amphoteric fixative polymer and anionic fixative polymer. When the combination of betainized amphoteric

fixative polymer and non-betainized amphoteric fixative polymer is selected, a mousse product with good foaming characteristics can be obtained with or without propellant. Such mousse product typically contains no more than about 30% volatile solvent in the composition.

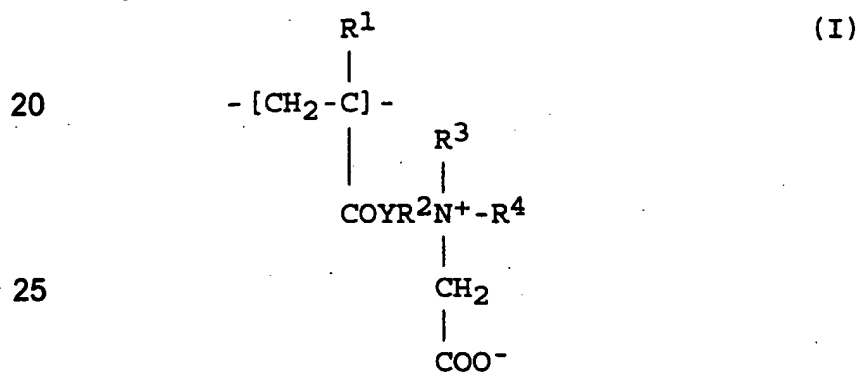
- 5        The fixative polymers are preferably included at a level of from about 0.01% to about 10% by weight of the composition. When two or more fixative polymers are used, the total preferably does not exceed about 10% by weight of the composition; more preferably, each fixative polymer does not exceed about 5% by weight of the composition.

#### 10    Amphoteric Fixative Polymer

The amphoteric fixative polymers useful herein include betainized amphoteric fixative polymers as described in (1) and (2) below, and non-betainized amphoteric fixative polymers as described in (3) and (4) below.

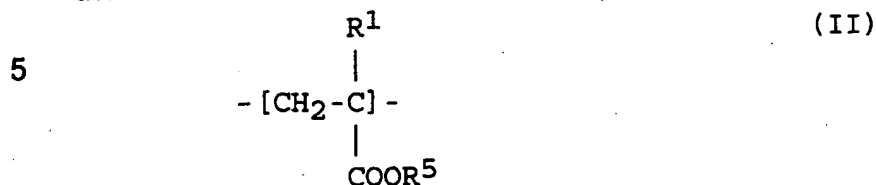
##### Betainized Amphoteric Fixative Polymers

- 15        (1) Useful herein are polymers of betainized dialkylaminoalkyl (meth)acrylate or dialkylaminoalkyl (meth)acrylamide containing at least units of the formula:



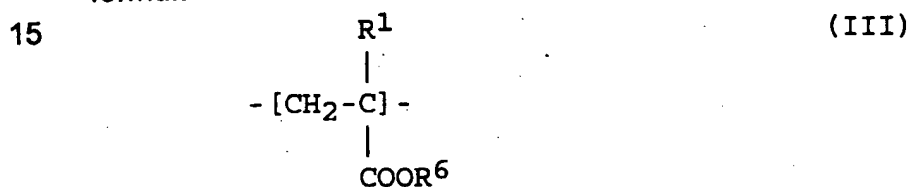
- 20        wherein R<sup>1</sup> denotes a hydrogen atom or a methyl group, R<sup>2</sup> denotes an alkylene group having 1 to 4 carbon atoms, Y denotes O or -NH- and R<sup>3</sup> and R<sup>4</sup> independently of one another denote hydrogen or alkyl having 1 to 4 carbon atoms, and one cationic derivative consisting of a cationic surfactant containing at least one nitrogen atom joined to one or more fatty chains and optionally quaternised, or consisting of a cationic polymer of the polyamine, polyaminopolyamide or poly-(quaternary ammonium) type, the amine or ammonium groups forming part of the polymer chain or being joined thereto.
- 25        These polymers usually have a molecular weight of 500 to 2,000,000.

The amphoteric polymers containing units corresponding to the above formula (I) are generally in the form of copolymers which contain, in addition to the units of the above mentioned formula (I), at least units of the formula:



10 wherein  $\text{R}^1$  is as defined above and  $\text{R}^5$  represents an alkyl or alkenyl radical having from 4 to 24 carbon atoms or a cycloalkyl radical having from 4 to 24 carbon atoms.

It is also possible to use terpolymers, tetrapolymers or pentapolymers which contain, in addition to the units (I) and (II) defined above, units of the formula:



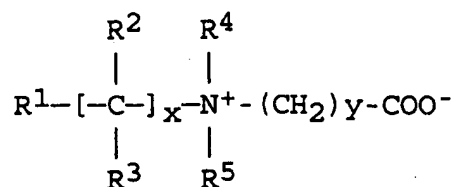
20 wherein  $\text{R}^6$  preferably denotes an alkyl or alkenyl group having 1 to 3 carbon atoms and  $\text{R}^1$  is as defined above.

The units of the formula (I) are preferably present in an amount of 25 to 45% by weight, units of the formula (II) are preferably present in an amount of 5 to 65% by weight, and units of the formula (III) are preferably present in an amount up to 50% by weight, relative to the total weight of the polymer.

25 A particularly preferred polymer is the copolymer containing units of the formulae (I), (II) and (III) in which Y denotes an oxygen atom,  $\text{R}^2$  denotes the group  $-\text{C}_2\text{H}_4-$ ,  $\text{R}^1$ ,  $\text{R}^3$  and  $\text{R}^4$  denote methyl,  $\text{R}^5$  denotes an alkyl group having 4 to 18 carbon atoms and  $\text{R}^6$  denotes an alkyl group having 1 to 3 carbon atoms.

30 The average molecular weight of this polymer is preferably from 50,000 to 100,000. This polymer is sold under the trademark "Yukaformer" or "Diaformer" supplied by Mitsubishi Chemical Corporation.

(2) Useful herein are the betainized polymers containing zwitterionic units derived from the formula:



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wherein R<sup>1</sup> denotes a polymerisable unsaturated group, such as an acrylate, methacrylate, acrylamide or methacrylamide group, x and y independently represent an integer from 1 to 3, R<sup>2</sup> and R<sup>3</sup> independently represent hydrogen, methyl, ethyl or propyl, and R<sup>4</sup> and R<sup>5</sup> independently represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R<sup>4</sup> and R<sup>5</sup> does not exceed 10.

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Highly preferred betainized amphoteric polymers include commercially available material such as YUKAFORMER SM, YUKAFORMER FH, YUKAFORMER 301, YUKAFORMER 204WL, YUKAFORMER 510, YUKAFORMER M-75, YUKAFORMER R250S, Diaformer Z-SM, and Diaformer Z-W supplied by Mitsubishi Chemical Corporation.

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#### Non-betainized Amphoteric Fixative Polymers

(3) Useful herein are the non-betainized amphoteric polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and -acrylamides.

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(4) Useful herein are the non-betainized amphoteric polymers containing units derived from

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- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quaternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

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The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

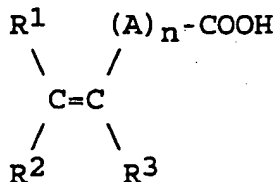
The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

Highly preferred non-betainized amphoteric polymers include commercially available material such as octylacrylamine/acrylates/butylaminoethyl methoacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

#### Anionic Fixative Polymer

The anionic fixative polymers useful herein include polymers containing units derived from carboxylic, sulphonic or phosphoric acid and usually have a molecular weight of 500 to 5,000,000. These polymers are water-soluble polymers, it being possible for this solubility to be obtained by neutralisation.

The carboxylic acid groups can be provided by unsaturated monocarboxylic or dicarboxylic acids, such as those corresponding to the formula:



wherein n is 0 or an integer from 1 to 10, A denotes a methylene group optionally joined to the carbon atom of the saturated group, or to the adjacent methylene group in the case where n is greater than 1, via a heteroatom, such as oxygen or sulphur, R<sup>1</sup> denotes a hydrogen atom or a phenyl or benzyl group, R<sup>2</sup> denotes a

hydrogen atom, a lower alkyl group or a carboxyl group and  $R^3$  denotes a hydrogen atom, a lower alkyl group,  $CH_2COOH$ , or a phenyl or benzyl group.

According to the invention, the preferred polymers containing carboxylic acid groups are:

5 (1) Homopolymers or copolymers of acrylic or methacrylic acid or salts thereof, and in particular, the products sold under the name VERSICOL E or K, and ULTRAHOLD by BASF and under the name DARVAN No. 7 by Van der Bilt; acrylic acid/acrylamide copolymers sold in the form of their sodium salt under the name RETEN 421, 423 or 425 by HERCULES; and the sodium salts of  
10 polyhydroxycarboxylic acids, sold under the name HYDAGEN F by HENKEL.

(2) Copolymers of acrylic or methacrylic acid with a monoethylenic monomer, such as ethylene, styrene, a vinyl or allyl ester or acrylic or methacrylic acid ester, optionally grafted onto a polyalkylene glycol, such as polyethylene glycol, and optionally crosslinked. Other such copolymers contain an optionally  
15 N-alkylated and/or N-hydroxylated acrylamide unit in their chain, such as those sold under the name QUADRAMER 5 by American Cyanamid.

(3) Copolymers derived from crotonic acid, such as those containing, in their chain, vinyl acetate or propionate units and optionally other monomers such as allyl or methallyl esters, a vinyl ether or a vinyl ester of a saturated linear or  
20 branched carboxylic acid with a hydrocarbon chain of at least 5 carbon atoms, if appropriate, for these polymers to be grafted and crosslinked, or also a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. Included in this class are those with the tradename RESYN 28-2930, 28-2913, and 28-1310 sold by National Starch & Chemicals.

25 (4) Polymers derived from maleic, fumaric and itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, such as those sold under the name GANTREZ A, SP, and ES by ISP. Other polymers included in this class are copolymers of maleic, citraconic and itaconic anhydrides with an allyl or methallyl ester optionally  
30 containing an acrylamido or methacrylamido group, or with an  $\alpha$ -olefine, acrylic or methacrylic acid ester, acrylic or methacrylic acid or vinylpyrrolidone unit in their chain; the anhydride groups can be monoesterified or monoamidified.

(5) Polyacrylamides containing carboxylate groups. Polymers comprising sulphonic groups include polymers containing vinylsulphonic, styrenesulphonic,

lignosulphonic or naphthalenesulphonic units. These polymers are chosen, in particular, from amongst:

- 5           i) Polyvinylsulphonic acid salts having a molecular weight of 1,000 to 100,000, and also copolymers with an unsaturated comonomer, such as acrylic or methacrylic acid or an ester thereof and also substituted or unsubstituted acrylamide or methacrylamide, vinyl esters, vinyl ethers and vinylpyrrolidone.
- ii) Polystyrenesulphonic acid salts, such as the sodium salt sold by National Starch & Chemicals under the name Flexan 500 and 130.
- 10          iii) Alkali metal or alkaline earth metal salts of sulphonic acids derived from lignin, and more particularly calcium lignosulphonates or sodium lignosulphonates, such as the product sold under the name Marasperse C-21 by American Can Co. and the C<sub>10</sub> to C<sub>14</sub> products sold by Avebene.
- 15          iv) Polymers containing salified alkylnaphthalenesulphonic acid units, such as the sodium salt under the name Darvan No. 1 by Van der Bilt.

20           The anionic hair fixative polymers herein which include anionic monomers are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. In the compositions the neutralisation of a polymer may be achieved by use of an inorganic base, preferably KOH. However organic base, preferably AMP (amino methyl propanol) and mixture of inorganic and organic base may also be used to effect the desired level of neutralisation in hair styling compositions. In total from  
25           about 50% to about 100%, preferably from about 70% to about 100%, most preferably from about 80% to about 100% of the acidic monomers of each polymer utilised should be neutralised with base.

          Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers provided they are utilised as specified herein.  
30           Hydroxides of alkali, alkaline earth and amino alcohols are suitable neutralisers.

          Examples of suitable organic neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1, 3-propanediol (AMPD), 2-amino-2-ethyl-1, 3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol  
35           (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA),



monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethylsteramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

5 Preferred neutralising agents for use in hair care compositions of the present invention are potassium and sodium hydroxides.

Highly preferred anionic fixative polymers include commercially available material such as vinyl acetate/crotonic acid/vinyl neodecanoate copolymers and vinyl acetate/crotonic acid copolymers with the tradenames RESYN 28-2930, RESYN 28-2913, and RESYN 28-1310 supplied by National Starch & Chemicals,  
10 and acrylates copolymers and acrylates/acrylamide copolymers with tradenames LUVIMER 100P, ULTRAHOLD 8, and ULTRAHOLD STRONG supplied by BASF Corporation.

#### Nonionic Fixative Polymers

The nonionic fixative polymers useful herein are homopolymer of  
15 vinylpyrrolidone or vinylcaprolactum and copolymers of vinylpyrrolidone with vinylacetate such as those with tradenames LUVISKOL K grades and LUVISKOL VA grades supplied by BASF Corporation.

#### Silicone Grafted Copolymers

The silicone grafted copolymers useful herein include those which have a  
20 vinyl polymeric backbone (A and B monomers), and grafted to such backbone a polydimethylsiloxane macromer (C macromer) having a weight average molecular weight of from about 1,000 to about 50,000. Preferably, these copolymers contain from and from about 50.0% to about 99.9% of the combination of A and B monomers, and from about 0.1% to about 50.0% of C  
25 macromer, wherein A is a lipophilic, low polarity free radically polymerizable vinyl monomer, such as methacrylic or acrylic esters; B is an anionic or nonionic hydrophilic polar monomer which is copolymerizable with A, such as acrylic acid, N,N-dimethylacrylamide, or vinyl pyrrolidone; and C is a silicone-containing macromer having a weight average molecular weight of from about 1,000 to  
30 about 50,000, based on polydimethylsiloxane. Preferred silicone grafted copolymers are those having a Tg above about -20°C, and a molecular weight of from about 10,000 to about 1,000,000.

Suitable silicone grafted copolymers herein include those listed below wherein the numbers indicate the weight ratio of monomers and macromers in  
35 the copolymer, silicone macromer S1 is a dimethylpolysiloxane having a

molecular weight of about 20,000, and silicone macromer S2 is a dimethylpolysiloxane having a molecular weight of about 10,000.

- 1) 20/63/17 acrylic acid/t-butyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 100,000
- 5 2) 10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 400,000
- 3) 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 400,000
- 4) 10/70/20 acrylic acid/t-butyl methacrylate/silicone macromer S1, having a  
10 copolymer molecular weight about 300,000
- 5) 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 200,000
- 6) 60/25/15 N,N'-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 200,000
- 15 7) 12/64/4/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000
- 8) 30/40/10/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight  
20 about 300,000
- 9) 80/20 t-butylacrylate/silicone macromer S2, having a copolymer molecular weight about 150,000

#### CARRIER

25 The styling composition of the present invention comprises a carrier. The level and species of the carrier are selected according to the compatibility with other components, and desired characteristic of the product. The styling compositions herein can be in any product form including, but not limited to, hair sprays, mists, mousses, gels, and creams.

30 The carrier useful in the present invention include water, volatile solvents, propellants, and mixtures thereof.

The water useful herein include deionized water and water from natural sources containing mineral cations. Deionized water is preferred.

Volatile solvents useful herein include lower alkyl alcohols having from 1 to 3 carbons, and hydrocarbons having from about 5 to about 8 carbons. The

preferred volatile solvents are, ethanol, isopropanol, pentane, hexane, and heptane

Propellants may be used for mousse and hair spray product forms. Propellants, when used in the present invention, are selected depending on  
5 variables such as the remainder of components, the package, and whether the product is designed to be used standing or invert.

Propellants useful herein include fluorohydrocarbons such as difluoroethane 152a (supplied by DuPont), dimethylether, and hydrocarbons such as propane, isobutane, n-butane, mixtures of hydrocarbons such as LPG  
10 (liquefied petroleum gas), carbon dioxide, nitrous oxide, nitrogen, and compressed air.

#### EMULSIFYING SURFACTANT

The styling composition of the present invention may include an emulsifying surfactant to disperse the water insoluble components in the carrier.  
15 Water insoluble components may include hydrophobic fixative polymers mentioned above, and hydrophobic thickening polymers, high melting point conditioning agents, and oily conditioning agents mentioned below.

The level and species of the emulsifying surfactant are selected according to the compatibility with other components, and desired characteristic of the  
20 product. Emulsifying surfactants are selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and mixtures thereof.

#### CONDITIONING AGENTS

The styling composition of the present invention may include a  
25 conditioning agent. Conditioning agents useful herein include high melting point compounds, oily compounds, silicone compounds, non-volatile solvents, and mixtures thereof.

#### High Melting Point Compound

The compositions may comprise a high melting point compound having a  
30 melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of  
35 combing. It is understood by the artisan that the compounds disclosed in this

section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol,

wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of  
5 ethylene glycol moieties present; C<sub>1</sub>-C<sub>30</sub> alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate,  
10 polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20  
15 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By  
20 "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein  
25 include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA),  
30 HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

#### Oily Compound

The compositions comprise an oily compound having a melting point of  
35 not more than about 25°C selected from the group consisting of a first oily

compound, a second oily compound, and mixtures thereof. The oily compounds useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair.

- 5 The oily compound may comprise either the first oily compound or the second oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International  
10 Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

#### First Oily Compound

- 15 The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl  
20 alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

- The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be  
25 straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

- The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl  
30 ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate,  
35 octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl

pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl  
5 alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a  
10 tradename ENUJERUBU series available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

#### Second Oily Compound

15 The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22  
20 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C<sub>2-6</sub> alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain  
25 lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable  
30 hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

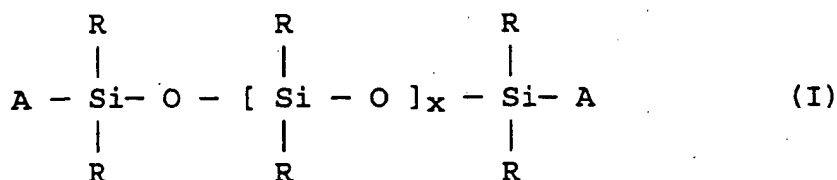
Commercially available second oily compounds useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA),  $\alpha$ -olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co., and trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co.

#### Silicone Compounds

The conditioning agents useful herein include silicone compounds. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone.

Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition,



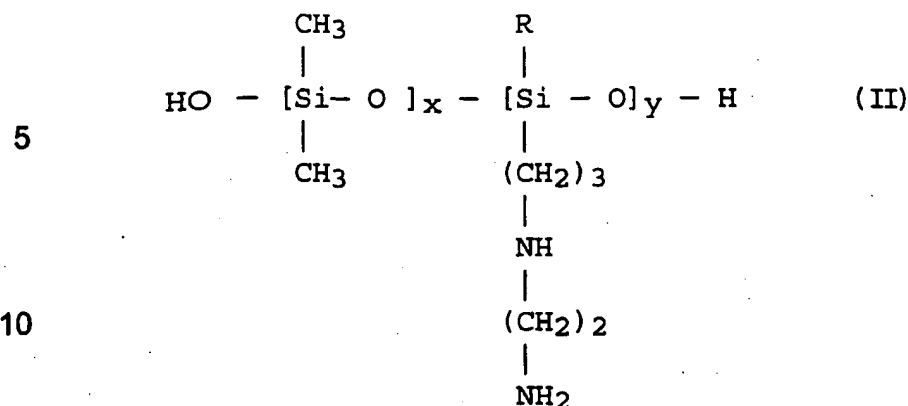
is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)



wherein R is CH<sub>3</sub> or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)

(R<sub>1</sub>)<sub>a</sub>G<sub>3-a</sub>-Si-(-OSiG<sub>2</sub>)<sub>n</sub>-(-OSiG<sub>b</sub>(R<sub>1</sub>)<sub>2-b</sub>)<sub>m</sub>-O-SiG<sub>3-a</sub>(R<sub>1</sub>)<sub>a</sub> (III)

20 in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a monovalent radical of formula C<sub>q</sub>H<sub>2q</sub>L in which q is an integer from 2 to 8 and L is chosen from the groups

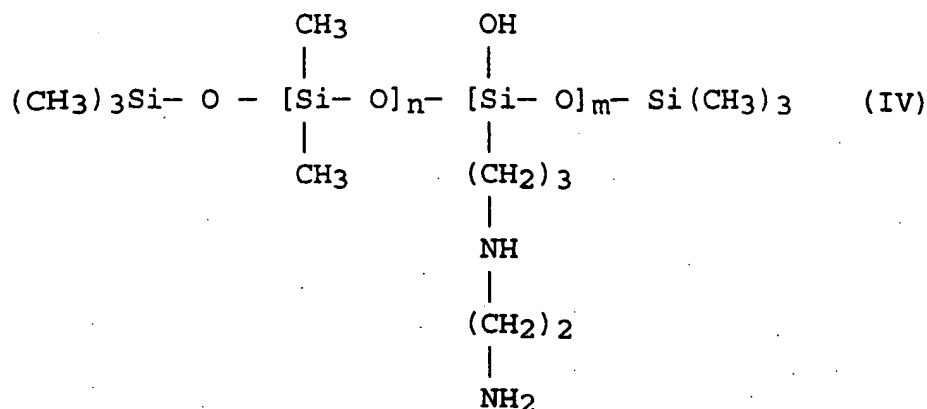
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- N(R<sub>2</sub>)CH<sub>2</sub>-CH<sub>2</sub>-N(R<sub>2</sub>)<sub>2</sub>
- N(R<sub>2</sub>)<sub>2</sub>
- N(R<sub>2</sub>)<sub>3</sub>A<sup>-</sup>
- N(R<sub>2</sub>)CH<sub>2</sub>-CH<sub>2</sub>-NR<sub>2</sub>H<sub>2</sub>A<sup>-</sup>

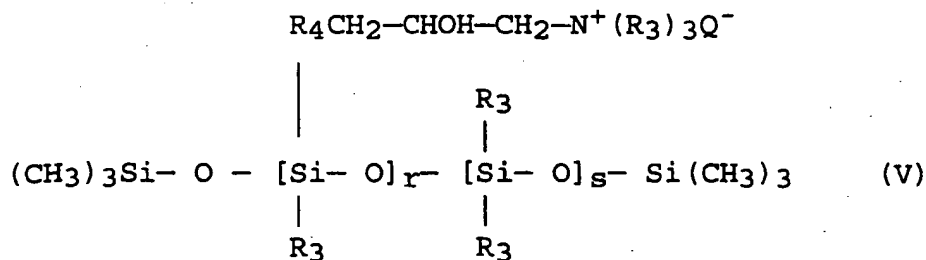
in which R<sub>2</sub> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A<sup>-</sup> denotes a halide ion.

35 An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



where  $\text{R}^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $\text{R}_4$  denotes a hydrocarbon radical, preferably a  $\text{C}_1 - \text{C}_{18}$  alkylene radical or a  $\text{C}_1 - \text{C}_{18}$ , and more preferably  $\text{C}_1 - \text{C}_8$ , alkyleneoxy radical;  $\text{Q}^-$  is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference

provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General

Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl<sup>TM</sup> from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit  $(\text{CH}_3)_3\text{SiO}_{.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl.

Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

#### Non-volatile solvents

5 Non-volatile solvents useful herein include alkyl alcohols having more than 3 carbons, and polyhydric alcohols. The polyhydric alcohols useful herein include 1,2-propane diol or propylene glycol, 1,3-propane diol, hexylene glycol, glycerin, diethylene glycol, dipropylene glycol, 1,2-butylene glycol, and 1,4-butylene glycol.

#### 10 THICKENING POLYMER

The compositions may include a thickening polymer. Thickening polymers are preferred for hair gel. When present, the thickening polymer functions as a viscosity-building agent, and can be distinguished from the fixative polymers mentioned above. The thickening polymer will generally comprise from about 15 0.1% to about 10.0%, and more typically from about 0.2% to about 3.0%, by weight, of the composition.

Useful thickening polymers herein include crosslinked carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which is 20 incorporated herein by reference in its entirety. Examples of these polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with an allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propylene. Other preferred thickening polymers include the cross-linked copolymers of methyl vinyl ether and maleic acid. Examples of these polymers 25 include Stabilezes. Preferred carboxyvinyl polymers have a molecular weight of at least about 750,000; more preferred are carboxyvinyl polymers having a molecular weight of at least about 1,250,000; most preferred are carboxyvinyl polymers having a molecular weight of at least about 3,000,000.

Other thickening polymers useful herein include those that can impart a 30 gel-like viscosity to the composition, such as water soluble or colloidal water soluble polymers like cellulose ethers such as hydroxyethyl cellulose and hydrophobically modified cellulose, and materials such as guar gum, xanthan gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives.

### ADDITIONAL COMPONENTS

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolyzed collagen with tradename Peptin 2000 available from Hormel, Vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate. Such optional ingredients generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

### **EXAMPLES**

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

#### Compositions

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8
Optical brightener1*1	0.20	-	-	-	-	0.10	0.10	0.10
Optical brightener2*2	-	0.25	-	-	-	-	0.10	-
Optical brightener3*3	-	-	0.50	-	-	-	-	-
Optical brightener4*4	-	-	-	0.20	-	-	-	0.25

Optical brightener5*5	-	-	-	-	1.00	0.10	-	-
Ultrasol 8*6	6.00	-	-	-	0.50	-	0.50	-
Luviskol VA 64*7	-	3.00	-	-	-	-	-	-
Amphomer LV71*8	-	-	2.00	-	-	-	1.50	0.50
Yukaformer R205*9	-	-	-	2.00	1.50	-	-	1.00
Silicone grafted copolymer 1*10	-	-	-	-	-	1.50	-	-
Aminomethyl propanol	0.15	-	0.30	-	0.04	-	-	-
Lauramide DEA	0.10	-	-	0.10	-	0.05	-	0.10
Triisopropylamine	-	-	-	0.10	-	-	0.05	-
Dimethicone Copolyol SH3746*11	0.10	-	0.05	-	-	-	-	0.05
Perfume	0.20	0.20	0.10	0.10	0.20	0.20	0.10	0.10
Deionized Water	20.0	45.5	20.0	45.0	21.0	46.0	20.0	20.0
Isobutane/ propane blend	-	25.0	25.0	-	15.0	15.0	-	20.0
Dimethyl ether	-	-	-	35.0	-	-	35.0	-
Hydrolyzed Collagen*25	0.01	-	-	-	-	-	-	-
Vitamin E*26	0.01	-	-	-	-	-	-	-
Panthenol*27	0.025	-	-	-	-	-	-	-
Panthenyl Ethyl Ether*28	0.225	-	-	-	-	-	-	-
Ethanol	----- q.s. to 100% -----							

	Ex.9	Ex.10	Ex.11	Ex.12	Ex.12	Ex.14	Ex.15	Ex.16
Optical brightener1*1	0.20	-	-	-	-	0.10	-	0.05
Optical brightener2*2	-	0.25	-	-	-	-	0.20	-



Optical brightener3*3	-	-	0.50	-	-	-	-	0.10
Optical brightener4*4	-	-	-	0.20	-	-	0.05	-
Optical brightener5*5	-	-	-	-	1.00	0.10	-	0.05
Ultrahold Strong*12	1.00	-	-	-	-	-	1.00	-
Luviskol VA 73W*13	-	1.00	-	-				
Amphomer 28-4910*14	-	-	4.00	-	3.00	-	2.50	1.00
Yukaformer 510*15	2.00	2.00	-	3.00	-	1.50	-	3.00
Silicone grafted copolymer 2*16	-	-	-	-	-	1.00	-	-
Aminomethyl propanol	0.15	-	0.70	-	0.50	-	0.45	-
Laureth-23	0.25	-	0.20	0.10	-	0.15	-	0.10
Laureth-7	-	0.20	0.10	0.10	0.20	-	-	-
Dimethicone Copolyol SH3746*11	0.10	-	-	-	-	-	0.05	-
DC BY22-009 *17	0.20	-	-	0.20	-	-	-	0.15
Propylene glycol	0.10	0.25	0.10	-	0.25	0.10	-	0.20
Methylparaben	0.15	0.15	0.10	0.10	0.15	0.15	0.10	0.15
Perfume	0.20	0.20	0.10	0.10	0.20	0.20	0.10	0.10
Ethanol	-	12.5	7.50	-	10.0	6.00	15.0	-
Isobutane/propane blend	6.00	8.00	7.00	10.0	8.00	8.00	7.00	-
Deionized Water	----- q.s. to 100% -----							

	Ex.17	Ex.18	Ex.19	Ex.20	Ex.21	Ex.22	Ex.22	Ex.24
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Optical brightener1*1	0.20	-	-	-	-	0.20	-	0.15
Optical brightener2*2	-	0.25	-	-	-	-	0.10	-
Optical brightener3*3	-	-	0.50	-	-	0.10	-	-
Optical brightener4*4	-	-	-	0.20	-	-	-	0.25
Optical brightener5*5	-	-	-	-	1.00	-	0.10	-
Gantrez ES-255*18	1.00	-	-	-	-	-	-	1.00
Luviskol K 30*19	-	2.00	-	-	3.00	-	-	-
Amphomer 28-4910*14	-	-	4.00	-	-	-	2.50	4.00
Yukaformer SM*20	2.00	1.00	-	3.00	-	1.25	1.50	-
Silicone grafted copolymer 2*16	-	-	-	-	-	1.25	-	-
Aminomethyl propanol	0.15	-	0.70	-	-	-	-	0.85
Carbopol 940*21	1.00	-	0.50	-	-	-	0.50	-
Stabileze 06*22	-	0.25	-	0.50	-	-	-	-
Cellosize HEC QP*23	-	-	-	-	1.50	-	-	-
Poly Surf 67*24	-	-	-	-	-	1.25	-	1.00
Sodium hydroxide	0.28	0.04	0.14	0.08	-	-	0.14	-
Laureth-23	0.25	-	0.20	-	0.25	0.15	-	0.10
Oleth-20	-	0.20	-	-	-	0.15	0.25	-
Dimethicone Copolyol SH3746*11	0.10	-	0.05	-	-	0.05	-	-

Methylparaben	0.15	0.15	0.10	0.10	0.15	0.15	0.10	0.15
Tetrasodium EDTA	0.10	0.05	0.10	0.10	-	0.10	0.10	0.10
Perfume	0.10	0.15	0.10	0.10	0.20	0.20	0.10	0.10
Ethanol	-	-	6.00	-	2.00	4.00	1.50	-
Deionized Water	----- q.s. to 100% -----							

**Definitions**

- \*1 Optical brightener 1: disodium-1,4-bis(2-sulfostyryl)bisphenyl with tradename Tinopal CBS-X available from Ciba Specialty Chemicals.
- 5 \*2 Optical brightener 2: disodium-4,4'-bis[[anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl]amino]stilbene-2,2'-disulfonate with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals.
- \*3 Optical brightener 3: 2-(4-styryl-3-sulfophenyl)-2H-naphto[1,2-d]triazole with tradename Tinopal RBS available from Ciba Specialty Chemicals.
- 10 \*4 Optical brightener 4: 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline
- \*5 Optical brightener 5: 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methoxyphenyl)-2-pyrazoline
- \*6 Ultrahold 8: Copolymer of acrylic acid, ethyl acrylate, and N-t-butyl acrylamide commercially available from BASF.
- 15 \*7 Luviskol VA64: Copolymer of vinylpyrrolidone and vinyl acetate, commercially available from BASF.
- \*8 Amphomer LV71: Copolymer of octylacrylamide, alkyl acrylates, butylaminoethyl methacrylate, commercially available from National Starch and Chemical Company.
- 20 \*9 Yukaformer R205: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.
- \*10 Silicone grafted copolymer 1: 20/63/17 acrylic acid/t-butyl methacrylate/silicone macromer S2, polymer molecular weight about 100,000
- 25 \*11 Dimethicone Copolyol SH3746: Polydimethylsiloxane with polyoxyethylene side chain.
- \*12 Ultrahold Strong: Copolymer of acrylic acid, ethyl acrylate, and N-t-butyl acrylamide, commercially available from BASF.

- \*13 Luviskol VA73W: Copolymer of vinylpyrrolidone and vinyl acetate, commercially available from BASF.
- \*14 Amphomer 28-4910: Copolymer of octylacrylamide, alkyl acrylates, butylaminoethyl methacrylate, commercially available from National Starch and Chemical Company.
- \*15 Yukaformer 510: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.
- \*16 Silicone grafted copolymer 2: 60/25/15 N,N'-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
- \*17 DC BY22-009: Silicone microemulsion commercially available from Dow Corning. \*1 Gantrez ES-225: Copolymer of vinyl methyl ether and ethyl ester of maleic acid, commercially available from ISP.
- \*18 Gantrez ES-255: Copolymer of vinyl methyl ether and ethyl ester of maleic acid available from ISP.
- \*19 Luviskol K30: Polyvinylpyrrolidone available from BASF.
- \*20 Yukaformer SM: Copolymer of methoacryloyl ethyl betaine and alkyl acrylates, commercially available from Mitsubishi Chemical Corporation.
- \*21 Carbopol 940: Cross-linked polyacrylic acid, commercially available from B.F. Goodrich.
- \*22 Stabileze 06: Cross-linked copolymer of methyl vinyl ether and maleic acid, commercially available from ISP.
- \*23 Cellosize HEC QP: Hydroxyethyl cellulose.
- \*24 Poly Surf 67: Hydrophobically modified hydroxyethyl cellulose commercially available from Aqualon Co.
- \*25 Hydrolyzed Collagen: Peptin 2000 obtained by Hormel
- \*26 Vitamin E: Emix-d obtained by Eisai
- \*27 Panthenol: available from Roche
- \*28 Panthenyl Ethyl Ether: available from Roche

#### Method of Preparation

The hair spray products of Examples 1 through 8 are suitably made as follows: Hair fixative polymer is dissolved in a portion of water and ethanol. In case an anionic fixative polymer such as Ultrahold 8 is used, it is neutralized with aminomethylpropanol in a portion of water and ethanol. To this is added the

remaining components except isobutane/propane blend. The obtained mixture is mixed until homogeneous. Finally, the concentrate thus obtained is packed into an aerosol can with isobutane/propane blend.

5 The hair mousse products of Examples 9 through 16 are suitably made as follows: Hair fixative polymer is dissolved in a portion of water. In case an anionic fixative polymer such as Ultrahold Strong is used, it is neutralized with aminomethylpropanol in a portion of water. To this is added the remaining ingredients except isobutane/propane blend. The obtained mixture is mixed until homogeneous. The concentrate thus obtained is packed into an aerosol can  
10 with isobutane/propane blend.

The hair setting gel products of Examples 17 through 24 are suitably made as follows: Carbopol 940 is dissolved in a portion of water. To this is added sodium hydroxide. In a separate container, the remaining components are dissolved in a portion of water. The two premixes are blended with agitation.

15 Examples 1 through 24 have many advantages. For example, they can be used daily, and provide color alteration, shininess, and UV protection to the hair.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light  
20 thereof will be suggested to one skilled in the art without departing from its spirit and scope.

## WHAT IS CLAIMED IS:

1. A hair styling composition comprising:
  - (a) an effective amount of an anionic optical brightener;
  - (b) a fixative polymer selected from the group consisting of an amphoteric fixative polymer, a nonionic fixative polymer, an anionic fixative polymer, a silicone grafted polymer; and mixtures thereof; wherein the 3% aqueous solution of the fixative polymer provides a viscosity of no more than about 2,000 cps; and
  - (c) a carrier.
2. The hair styling composition according to Claim 1 wherein the anionic optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, coumarins, triazoles, pyrazolines, and mixtures thereof;
3. The hair styling composition according to Claim 1 comprising by weight from about 0.001% to about 20% of the anionic optical brightener and from about 0.01% to about 10% of the fixative polymer.
4. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of a betainized amphoteric fixative polymer; and from about 0.1% to about 5% of a non-betainized amphoteric fixative polymer.
5. The hair styling composition according to Claim 3 wherein the fixative polymer comprises by weight from about 0.1% to about 5% of an amphoteric fixative polymer; and from about 0.1% to about 5% of an anionic fixative polymer.

6. The hair styling composition according to any of Claims 1 through 5 further comprising an emulsifying surfactant.
7. The hair styling composition according to any of Claims 1 through 5 further comprising a conditioning agent.
8. The hair styling composition according to any of Claims 1 through 5 further comprising a thickening polymer.
9. The hair styling composition according to Claim 4 wherein the composition comprises no more than 30% volatile solvent, and wherein the composition is substantially free of propellant.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/13 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 312 855 A (GRAND PAUL S) 26 January 1982 cited in the application see column 1, line 9-20 see column 2, line 11-64 see column 5, line 45 - column 6, line 14; claims; example 11; table III	1-3, 6-9
Y	GB 2 307 639 A (GEN ELECTRIC) 4 June 1997 cited in the application see claims 1-4 -/--	1-9

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"Z" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/16315

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	GB 1 328 108 A (UNILEVER LTD) 30 August 1973 cited in the application see page 1, line 10-17 see page 1, line 65-92; claims 1,6 ---	1-9
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Y	WO 97 18795 A (OREAL ;AUDOUSSET MARIE PASCALE (FR); MONDET JEAN (FR)) 29 May 1997 see page 4, line 28-32; claims; example 2 -----	1-9

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